Micromorphological Studies of the Corrosion of Gold Alloys

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Considerable insight into the detailed mechanisms by which metals are corroded can be derived from direct microscopic observations. This article describes those micromorphological changes occurring near the surface that can be observed by transmission electron microscopy after gold alloys have been subjected to anodic dissolution in strong acids. These observations are used to discuss the important problem of corrosion by selective dissolution.

Direct observation of the surface of a metal after exposure to a corrosive environment has frequently been used as a basis for deductions concerning the structural processes by which chemical reactions modify the surface and near-surface layers. Although considerable information can be obtained in this way using simple optical microscopy, as, for example, in the case of the aqueous corrosion of gold-copper alloys studied by Graf (1), Bakish and Robertson (2) and Pickering (3), a much more detailed picture can be obtained with the electron microscope, particularly when this is coupled with the powerful analytical techniques of selected area electron diffraction and X-ray microanalysis. The availability of very high resolution microscopes now makes it possible to follow changes in the internal microstructure, the surface morphology and the composition of metals and alloys on a scale approaching atomic dimensions.

The use of the transmission electron microscope necessitates the study of very thin specimens. Great care must be taken to ensure that the micromorphological changes arising from corrosion can be distinguished from those produced during the preparation of such thin films from bulk samples. For this reason, there may be doubts concerning the validity of some of the observations by Pickering and Swann (4) and by others who have studied the corrosion of alloys prepared as thin foils by electropolishing techniques. Ion-sputtering methods for thinning alloys from bulk specimens may also be suspect, because different sputtering rates for the various constituents can lead to compositional changes. These difficulties have been largely overcome recently by Durkin and Forty (5) who have developed techniques for preparing thin films by vapour deposition of an alloy from its individual components. It will be shown later how this has contributed to a very detailed understanding of the corrosion micromorphology in the special case of gold-silver alloys.

Selective Dissolution

The most widely studied and possibly the most important phenomenon involved in the aqueous corrosion of gold alloys is that of selective dissolution, whereby the less noble element is preferentially removed from the alloy, leaving a gold-rich residue (6). This is the basis of various practical methods for the parting gold from its alloys. It is also thought to be an important step in the stress corrosion of gold alloys since rupture of the gold-rich surface layer by an applied stress can lead to the initiation of localized, deeper corrosion and subsequently of a stress corrosion crack (1, 2, 3). As we shall discuss later, selective dissolution might also be an important precursor of other corrosion reactions, such as oxidation.

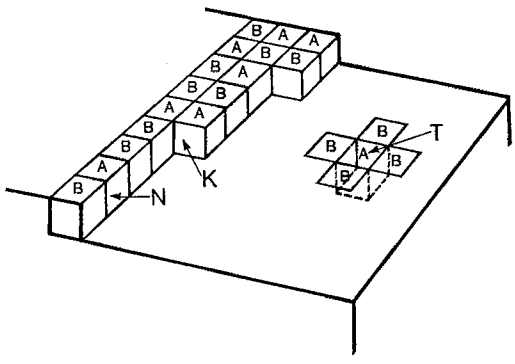

Fig. 1 Schematic representation on an atomic scale of the surface of an alloy composed of dissolvable A atoms and noble B atoms.
K is a kink site on a surface step
N is a non-kink site on a step
T is a terrace site

The fundamental question to be answered, as far as the understanding of selective dissolution is concerned, is why a gold-based alloy should continue to dissolve in this way beyond the stage where the surface should be passivated by the gold residue. Such passivation might be expected to develop at a very early stage, as can be seen from a consideration of the atomic processes that might be occurring on the metal surface during dissolution. These are depicted in their simplest form in Figure 1, where we ignore molecular adsorption, oxidation and complexing effects associated with the electrolyte, and assume that dissolution involves only ionization and solvation of the metal atoms. Dissolution is expected to occur preferentially from kink sites (K) in the surface steps where the atoms are least firmly bound and, at sufficiently low potentials, the dissolution current will involve predominantly A atoms — the less noble species. As dissolution proceeds, however, this current will be diminished as more and more kink sites become occupied by more noble B atoms. Thereafter, dissolution can proceed only by the removal of A atoms from non-kink sites (N) on steps or from terrace sites (T), which requires a greater activation energy or overpotential. Eventually, the alloy becomes completely passivated when all the surface sites are occupied by B atoms only. For most alloys, and Cu_3Au in particular, this passivation stage should be reached after the removal of A atoms from only a few atomic layers. This is clearly contrary to practical experience, from which we must infer that this simple model of selective dissolution is incorrect.

The continuing dissolution of the alloy must mean that some form of mass transport accompanies the corrosion reaction in such a way as to expose more of the less noble, dissolvable atomic species at the surface. There are three possible mechanisms for this. One is an electrochemical transfer of gold from more anodic to cathodic sites on the surface, so that fresh alloy is continuously exposed to the environment in the anodic regions. However, on thermodynamic grounds, it is doubtful whether this process is generally applicable (7), particularly in the case of gold alloys where a highly noble species is involved. Nevertheless, it has been suggested (8) that such a process might be involved in the formation of corrosion tunnels. However, as we shall see later, there is an alternative explanation for this. Another possibility is that the less noble component is continuously replenished at the surface by volume diffusion from the underlying layers of alloy. The relatively high diffusion flux required to support the dissolution current can be accounted for by an inward flow of lattice vacancies generated at the surface by selective dissolution from individual atomic sites. There is considerable support for this model from measurements of partial dissolution currents and changes of surface potential, particularly in the case of gold-copper alloys which Pickering and other workers (9, 10) have studied extensively. Pickering (11) has also shown, using a reflection X-ray diffraction technique, that changes of lattice parameter detected in the near-surface layers of gold-copper alloys are consistent with an accumulation of vacancies injected during selective dissolution. An additional possible mechanism by which fresh alloy may be continuously exposed to the corrosive medium is by surface diffusion of the residual gold atoms so that they form islands of noble metal on the alloy surface. This has been shown to be an important factor in the development of corrosion micromorphology by the recent work on gold-silver alloys by Forty and Durkin (12). In a later section of this article it will be suggested that both volume diffusion and surface diffusion are of importance in the corrosion reaction. There is an initial step in which vancancies diffuse to form a disordered zone near the surface, this process being possibly accompanied by an oxidation reaction. This metastable region then decomposes into gold-rich islands which grow by surface diffusion. It will be shown that the growth and coalescence of these islands lead to the formation of pits and eventually corrosion tunnels.

Corrosion Tunnelling

The first observations of corrosion tunnels were made by Nielsen (13) on stainless steels exposed to hot chloride solutions. By examining oxide replicas of the surface of such specimens in the transmission electron microscope, he was able to reveal the existence of long tunnels of sub-microscopic dimensions which penetrated the metal along slip bands and other structural singularities. Nielsen interpreted these features as localized corrosion tunnels formed by the dislocation lines. We shall see later that this localization of the attack along dislocation lines is not a necessary feature of tunnelling, which is a more general form of corrosion associated with imperfections in passivating surface films or with any other preferentially anodic site.

The occurrence of corrosion tunnels in gold alloys was first reported by Pickering and Swann (4). These authors used transmission electron microscopy to examine the micromorphology of thin foils of various gold-copper alloys directly after exposure to various corrosive environments. Since the foils were prepared by electropolishing of thicker specimens, great care was taken to avoid introducing corrosion damage artificially prior to exposure. It was found that the dominant form of corrosion morphology consisted of closely spaced pits or tunnels, depending on the composition of the alloy and the nature of the corroding

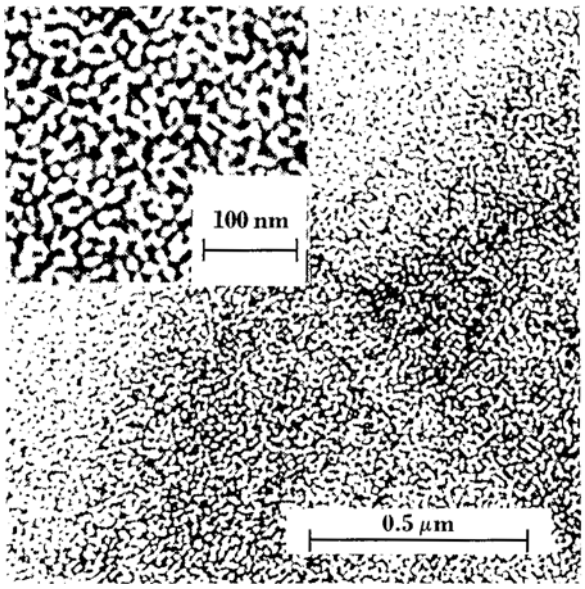

Fig. 2 A colony of corrosion tunnels in a gold-copper alloy film after corrosion in ferric chloride solution. This transmission electron micrograph was published by Pickering and Swann (4)

reagent. Figure 2 is a typical example of a colony of tunnels formed in the 25 gold/75 copper atomic per cent alloy by immersion in aqueous ferric chloride solution. It is particularly interesting that environments such as ferric chloride solution, known to promote stress corrosion cracking, produce deep corrosion tunnels, whereas other environments which do not induce such cracking, potassium cyanide solution for example, give only shallow pits. It was found that when tunnelling occurred, the tunnel radius varied significantly with alloy composition, ranging from approximately 4 nm for gold/95 copper atomic per cent to 30 nm for the 40 gold/60 copper alloy.

Swann and various co-workers (14) have subsequently extended these observations to other alloy systems, including stainless steels in hot magnesium chloride solution and gold-nickel in ferric chloride. Once again, they demonstrated that corrosion tunnelling is commonly found under conditions known to lead to stress corrosion cracking in these alloys. This has led to a model for transgranular stress corrosion, in which the porous material formed by tunnelling corrosion along active slip bands is ruptured by the applied stress to initiate a propagating crack.

Swann (15) has examined the conditions under which a corrosion tunnel might form. He suggests that a small depression in the surface of an alloy is sufficient to establish a stable tunnel if selective dissolution occurs, so that the side-walls become fully protected by the accumulation of atoms of the more noble species. It is implicit in this suggestion that the noble component is deposited on the side-walls, probably by surface diffusion or by ionization and re-deposition. It can easily be shown that this leads to a simple geometrical criterion for tunnelling to occur:

$$R_c = 2d(1-c)/c$$

where R_c is the critical tunnel radius, d is the thickness of an atomic layer and c is the atomic fraction of noble metal atoms in the alloy. If the tunnel radius is smaller than R_c, the side-walls are not sufficiently protected by the deposited gold atoms and the tunnel will widen by anodic dissolution. At larger radii, sufficient gold atoms will be deposited to cause the tunnel to shrink back to the critical size.

Despite its attractiveness in providing a simple qualitative description of tunnelling, Swann's model fails to account quantitatively for the sizes of tunnels observed under the electron microscope, as can be seen from the comparison of measured and calculated radii given in Table I. Swann (15) has argued that this large discrepancy is the result of a tendency for the redeposited gold to aggregate into small particles on the tunnel walls rather than form a uniform protective layer, and he has produced electron microscope images which suggest that such particles do exist. The formation of particles means, of course, that the tunnels must grow to radii greater than R_c before the side-walls can be fully passivated by a continuous gold deposit. Recent observations by Forty and Durkin (12) on gold-silver alloys (described in the next section) have shown that selective dissolution of silver leads to the growth of gold islands on the surface of the corroded alloy and that the tunnelling morphology develops as a result of the coalescence of neighbouring islands. We shall show later how this leads to an alternative model which gives calculated values of R_c which are in much better agreement with microscopic observations.

Table I
Observed and Calculated Values of the Radii of Stable Corrosion Tunnels in Various Gold Alloys. After (15) and (17)

Alloy, at. per cent	Exp. R_c, nm	Calc. R_c (17), nm	Calc. R_c (15), nm
50 Au/50 Ag	28	30	
33 Au/67 Ag	26	25	
5 Au/95 Ag	4	5	
25 Au/75 Cu	10	15	1
40 Au/60 Cu	30	40	0.5
16 Au/84 Ni	4.5	5	

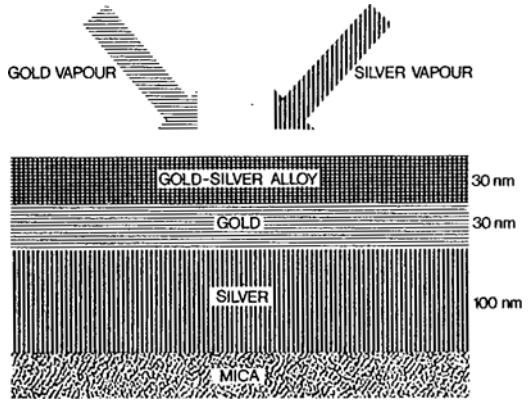

Fig. 3 Method used by the author and his co-workers for preparing thin single crystal films of gold-silver alloys for micro-corrosion experiments

Surface Island Growth

Swann's observations described in the preceding section were made on thin foils prepared from bulk alloys by electropolishing. This technique produces surfaces which may be rough at the atomic scale and contaminated by films of oxide or some other residues of electrochemical reactions. These surfaces are therefore not ideal for fine studies of the microscopic structural changes that might occur during a corrosion reaction. For this purpose, smooth, crystallographically well-defined surfaces, free from an initial oxide layer are required. Surfaces of this high quality have been produced on gold-silver alloys by Durkin and Forty (5), using the technique of vapour deposition. The procedure is illustrated schematically in Figure 3. First, a layer of silver, about 100 nm in thickness, is deposited at a rate of about 0.5 nm/s onto a freshly cleaved mica surface held at 285°C. The silver deposits epitaxially on the mica, so that a clean single crystal surface in a (111) plane orientation is obtained. Next, an intermediate 30 nm thick layer of pure gold is deposited epitaxially on the silver at the rate of 0.1 nm/s, and this is followed immediately by a further layer of 30 nm of alloy, formed by evaporating from the silver and the gold sources simultaneously at appropriate rates. Thus, the 50 gold/50 silver atomic per cent alloy is formed if both silver and gold are deposited at 0.1 nm/s; the 25 gold/75 silver per cent alloy requires deposition rates of 0.1 nm/s for gold and 0.3 nm/s for silver. The pure gold intermediate layer, together with its coating of alloy, is then detached from the mica by floating onto a bath of dilute nitric acid so that the initial layer of silver is slowly dissolved. The intermediate layer of pure gold functions as a buffer to prevent corrosion of the alloy during this operation.

The resulting film is a single crystal of alloy on a gold base with its surface in a well-defined (111) crystallographic orientation. The specimen can be exposed to a corrosive environment and then examined directly in the electron microscope. All the observations reported in this and the following sections were made on samples prepared in this way. We describe here our work on gold-silver alloys, but a similar technique is currently also being used to examine the corrosion morphology of gold-copper and gold-nickel alloys (16).

The gold-silver system in nitric acid is particularly useful as a model for micromorphological studies of corrosion by selective dissolution. Silver and gold alloy substitutionally as a single face-centred cubic (fcc) phase across the complete compositional range. The pure metals and all the alloys have almost identical crystal lattice parameters, and this means that there is very little lattice strain, and consequently no significant microstructural effect, arising from lattice parameter changes during selective dissolution. Furthermore, because of the high solubility of silver nitrate, there should be no insoluble corrosion product. (However, as will be shown later, there is some evidence that gold oxide forms during the selective dissolution of silver.) Thus, changes in micromorphology observed after corrosion may be interpreted simply on the basis of the various forms of mass transport by which the alloys respond to selective dissolution. It is not possible to draw such unambiguous conclusions from microscopic studies of gold-copper alloys where lattice parameters change extensively and several structural ordering processes may occur when the composition varies.

The most striking conclusion from microscopic studies of a wide range of gold-silver alloys prepared as described above and corroded in nitric acid of various strengths, is that there is an extensive rearrangement of the initially smooth surface leading to the formation and growth of small, gold-rich islands (12). An example of this is to be seen in Figure 4 in electron micrographs of a 50 gold/50 silver atomic per cent alloy film recorded after exposure for two successive periods to 50 per cent aqueous nitric acid. Figure 4(a) shows a group of islands formed after an initial exposure to the acid of 30 s and Figure 4(b) shows the same field of view after a further exposure of another 30 s. Considerable growth of the islands as a result of the more prolonged exposure is evident from a comparison of these two micrographs. Eventually the islands coalesce and form a continuous gold network extending across the surface of the specimen. The corrosion is then reduced to localized activity within the channels and pits, formed as a result of incomplete coalescence of the gold islands. These channels and pits begin to deepen as their diameter

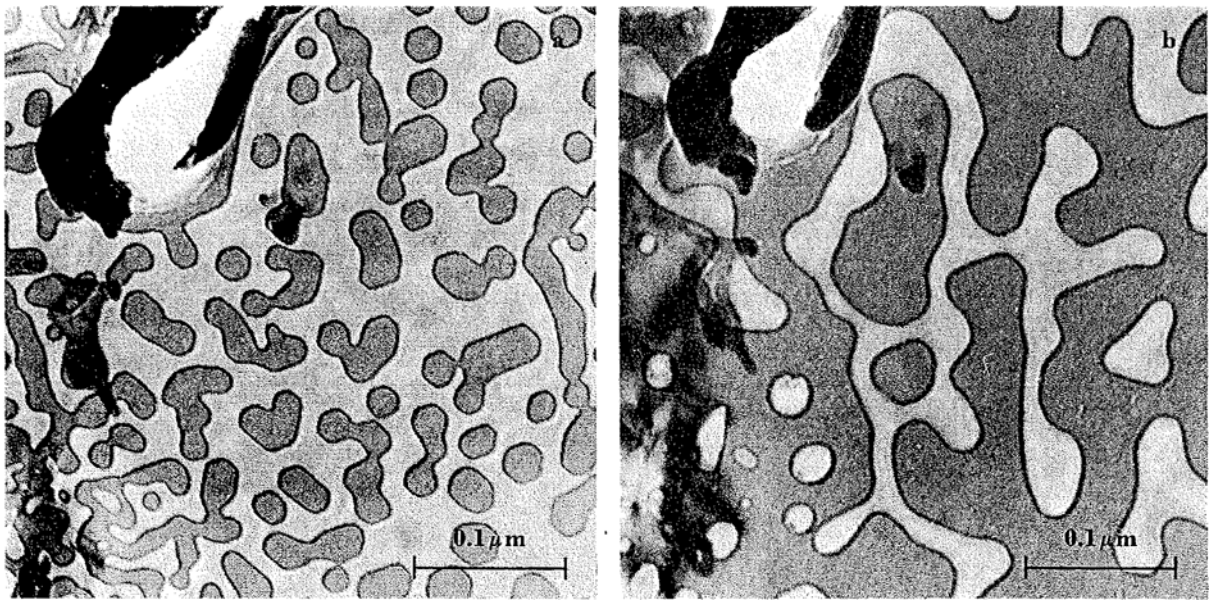

Fig. 4 Illustrating the formation and growth of islands during the corrosion of a 50 gold/50 silver atomic per cent alloy film in 50 per cent nitric acid solution, (a) is a transmission electron micrograph of the specimen after immersion in acid for 30 s and (b) is the same field after immersion for a further 30 s. After (12)

continues to shrink until a form of tunnelling morphology is reached. The transmission electron micrograph in Figure 5 shows this last stage in the corrosion of a 30 gold/70 silver atomic per cent alloy in concentrated nitric acid. The tunnelling morphology so produced is very similar to that found for gold-copper alloys corroded in ferric chloride solution by Pickering and Swann, and illustrated in Figure 2.

The process of island growth leading to pit and tunnel formation is accelerated if stronger acid is used or if the silver content of the alloy is increased. This can be seen by comparing the examples of Figure 4 and Figure 5. In the latter case, the increased amount of silver and the use of concentrated nitric acid have led to the final stage of tunnelling, while in the former only the coalescence stage of island growth has been reached. Further growth of the islands and pit formation can also be produced by annealing the corroded specimens at approximately 450°C as shown in Figure 6. This observation suggests that the corrosion reaction, which is almost certainly accompanied by the selective dissolution of silver, leaves the alloy surface in a highly disordered state which then re-orders by thermally-activated surface diffusion of the residual gold atoms into island structures. The extent of the disorder, and hence the rate of re-ordering, are dependent on the silver concentration and the strength of the acid. It is thought that the corrosion-induced disordering and the diffusion-controlled re-ordering occur continuously, so that the islands have an increasing passivating effect as they spread across the surface, and the corrosion reaction therefore becomes confined to the channels between the islands, and ultimately is concentrated at the pits remaining after coalescence. The expected sequence of

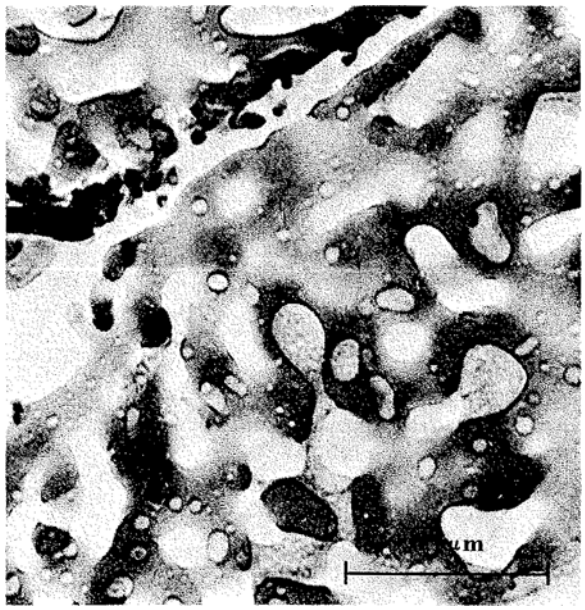

Fig. 5 Tunnelling corrosion in a 30 gold/70 silver atomic per cent alloy film after exposure for 30 s to concentrated nitric acid. After (12)

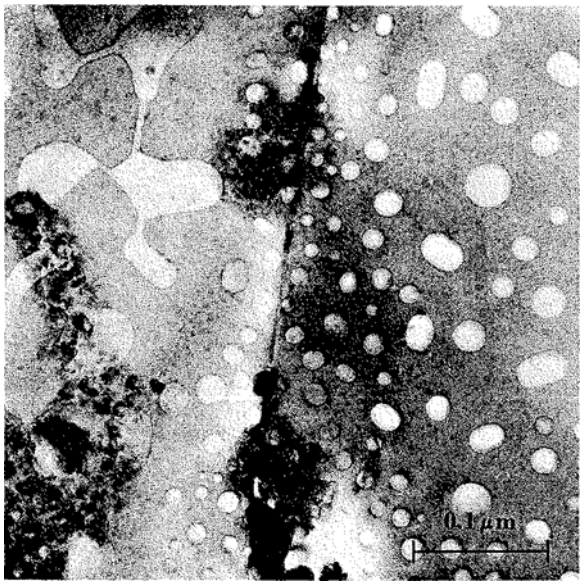

Fig. 6 Enhanced growth of gold islands on the surface of a sample of corroded 50 gold/50 silver atomic per cent alloy after annealing for 30 s at 450°C. After (12)

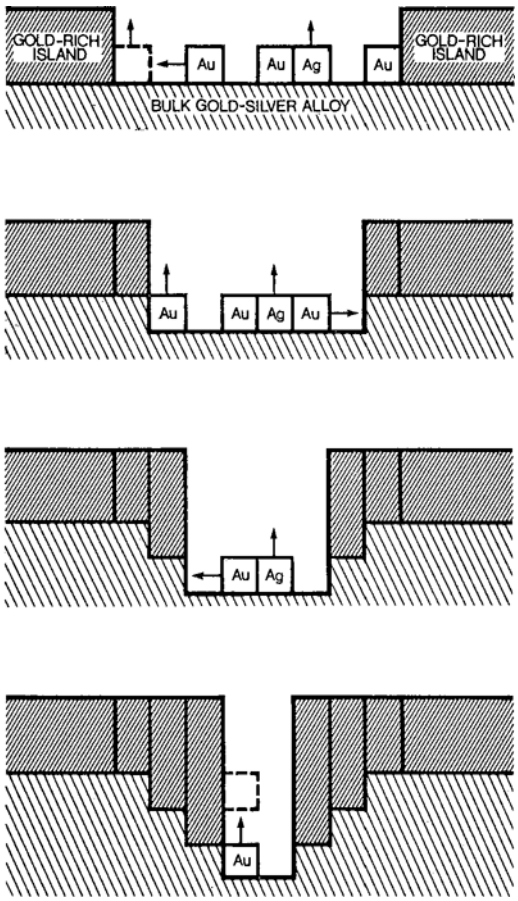

Fig. 7 The corrosion-disordering/diffusion-reordering model of corrosion by selective dissolution. After (17)

events is represented schematically in Figure 7. It is interesting that the island-channel-pit morphology is found only for alloys containing between 20 and 50 atomic per cent gold. This can be accounted for on the basis of our model because, in the silver-rich alloys, island nucleation is difficult due to the relatively small concentration of residual gold atoms, whereas, in the gold-rich alloys, the residual atoms, being more densely packed, migrate across the surface less easily. However, as we shall show in the last two sections of this article, the occurrence of the island morphology might be dependent on an intermediate stage of oxidation of gold during selective dissolution of silver, and this might form only for the alloys containing 20 to 50 atomic per cent gold.

This simple model of corrosion, based on selective dissolution and surface diffusion, has been examined more quantitatively by Forty and Rowlands (17). It can be seen from Figure 7 that gold accumulates in ever increasing thicknesses as the islands spread across the surface. This, together with the restriction of the occurrence of further corrosion to the channels between islands, means that these channels shrink at a continuously decreasing rate. As the islands coalesce, the channels break up into isolated pits which then continue to deepen at an accelerated rate while they shrink inwards more and more slowly. The results of a detailed analysis of the kinetics of pit shrinkage based on this model are given in Figure 8. We see that for alloys having a low gold concentration the pits shrink at progressively lower rates and never completely fill in — that is, the surface is never completely passivated. For gold-rich alloys (over 50 atomic per cent gold), pits are filled in after a finite time, which decreases as the gold content of the alloys increases. There is a critical alloy composition with 50 per cent gold below which the pits shrink at an exponentially decreasing rate. Thus, we find from this simple model that there is a 'parting limit' such that only those alloys containing less than 50 atomic per cent gold will continue to undergo selective dissolution if surface diffusion is the controlling mass transport process. This is in reasonable agreement with the parting limit of between 30 and 50 atomic per cent gold observed in practice (18).

A New Model for Corrosion Tunnelling

The calculations of Forty and Rowlands (17) also show very clearly how the quasi-stable pits formed by island coalescence on dilute gold alloys (of less than 50 atomic per cent gold) lead eventually to a tunnelling morphology. Figure 9 shows, for example, the calculated profile for a pit in a 33 gold/67 silver atomic per cent alloy formed by the corrosion-disordering/diffusion-reordering process. As the pit shrinks, it reaches a critical radius when it begins to

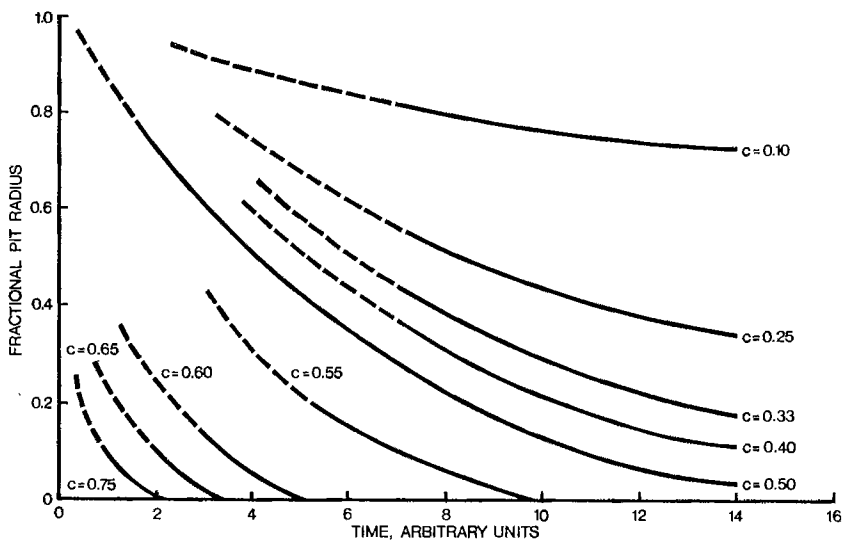

Fig. 8 Shrinkage of corrosion pits on a range of gold/silver alloys calculated on the basis of the corrosion-disordering/diffusion-reordering model. c is the atomic fraction of gold in the alloys. After (17)

deepen faster than its radius contracts and eventually it becomes a deep tunnel the radius of which then changes only very slowly with depth. Since the depth of such a pit is essentially a linear function of corrosion time, the profile shown in Figure 9 can also be interpreted as describing the development of a pit with time.

The transmission electron micrograph shown in Figure 10 gives an example where the transition from the island-channel-pit morphology to a tunnelling morphology is taking place for the 33 gold/67 silver atomic per cent alloy corroded in 30 per cent aqueous nitric acid. Where isolated pits have been formed, the penetration of the alloy has occurred at an accelerated rate, as can be seen from the enhanced transparency of these regions.

The critical radius, R_c, at which the rate of penetration of a pit begins to exceed the rate of shrinkage of its diameter, corresponds to the stage at which the amount of gold released by selective dissolution of silver from a monolayer of alloy at the bottom of the pit is only just sufficient to give monolayer coverage of the side-walls after diffusion. This leads to the geometrical condition:

$$R_c = 2N_c d/c$$

where N_c is the pit depth, measured in number of alloy monolayers of thickness d, and c is the atomic fraction of gold in the alloy. N_c is dependent on the composition of the alloy and on the initial distribution of the gold islands, and thus R_c is a complex function of c.

Values of R_c calculated on the basis of this new model are given in Table I where they can be compared with the observed radii of tunnels for various gold alloys together with the critical radii calculated from Swann's model. Thus, we see that the island-channel-pit model, evolved directly from microscopic observations of corroded surfaces, is not only more

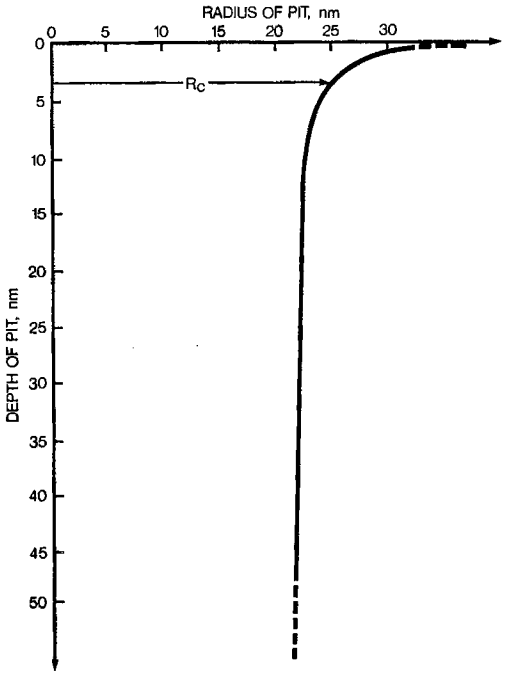

Fig. 9 Expected profile of a corrosion pit on a 33 gold/67 silver atomic per cent alloy calculated on the basis of the corrosion-disordering/diffusion-reordering model

realistic than Swann's model, but is also more successful in accounting quantitatively for the measured radii of corrosion tunnels. Although island growth has been observed for gold-silver alloys and, under certain circumstances, has also been found on gold-copper alloys, it has not so far been found on gold-nickel alloys. However, the close correspondence of calculated and observed tunnel radii found for all the gold alloys which are listed in Table I suggests that island growth might be a common occurrence for all such alloys.

A corrosion tunnel can be expected to penetrate the alloy indefinitely. Branching into secondary tunnels might occur at structural inhomogeneities and consequently the final morphological state will consist of a labyrinth or interconnected porous structure. Tunnels can occur preferentially at grain boundaries, slip bands and other microstructural features such as twin boundaries. Thus, corrosion tunnelling leads eventually to the disintegration of the solid alloy. This can occur even in the highly perfect single crystal films used for the study of island growth, because these films appear to be damaged by the corrosion reaction. The electron micrograph in Figure 11 shows, for example, the progressive disintegration of a single crystal of the 25 gold/75 silver atomic per cent alloy after a prolonged immersion in dilute nitric acid. The initial corrosion by selective dissolution produces islands on the surface and at the same time an extensive network of narrow twins is developed within the alloy. The islands grow preferentially along the surface traces of these twins, so that narrow corrosion channels form along these directions. Once the channels reach the critical width for tunnelling, which is close to the critical radius for a cylindrical tunnel, they penetrate the alloy very rapidly, so that it crumbles into small particles, as seen in Figure 11(a). The electron diffraction pattern for the alloy in this state is given in Figure 11(b), which shows how the residual granules have become separated and misorientated into a polycrystalline powder. It is probable that further selective dissolution of silver from these particles leads to the so-called gold-rich 'sludge' commonly found after alloy parting (6).

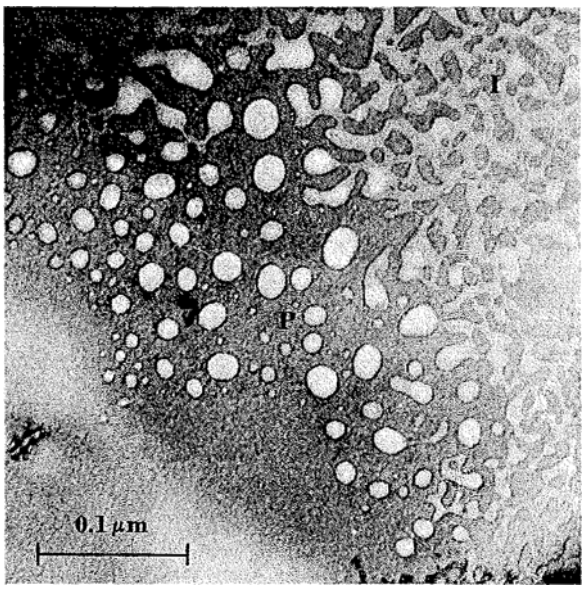

Fig. 10 Transmission electron micrograph of a 33 gold/67 silver atomic per cent alloy film corroded in dilute nitric acid, showing the transition from the island-channel morphology (I) to a deep pit morphology (P)

The Micro-Mechanisms of Corrosion Disordering

From their electron microscope observations of corroded gold-silver alloys, Forty and Durkin (12) have deduced that the selective dissolution of silver leaves the surface in a highly disordered state which subsequently recovers by surface diffusion to form gold-rich islands. Very recent work by the author (unpublished) has shown that corrosion disordering occurs in a near-surface zone, approximately 5 nm thick, by a complex sequence of processes involving selective dissolution, oxidation of the residual gold and finally the decomposition of oxide back into gold.

The evidence for this comes from a detailed analysis of the electron diffraction patterns and high resolution electron micrographs obtained from corroded alloys. Figure 12 shows the electron diffraction patterns obtained for a 25 gold/75 silver atomic per cent alloy before and after corrosion in dilute nitric acid. We see that the corrosion reaction has produced a new phase which gives rise to the extra diffraction spots apparent in Figure 12(b). This new phase can be revealed by dark field electron microscopy using the extra spots to form the image that is shown in Figure 13(b). Figure 13(a) is the normal bright field image of this area. The dark field image features a strongly diffracting phase, corresponding to the extra spots in the diffraction pattern, which covers the surface of the corroded alloy in well-defined domains. From dark field images of this kind, using all the extra diffraction spots in turn, we deduce that there are three distinct sets of such domains corresponding to the three-fold symmetry in the diffraction pattern. The crystallographic character of the domains is apparent in Figure 14 which is a high resolution image formed by the interference of beams doubly diffracted by the uncorroded underlying alloy and the corrosion phase. The moiré pattern thus produced, consists of

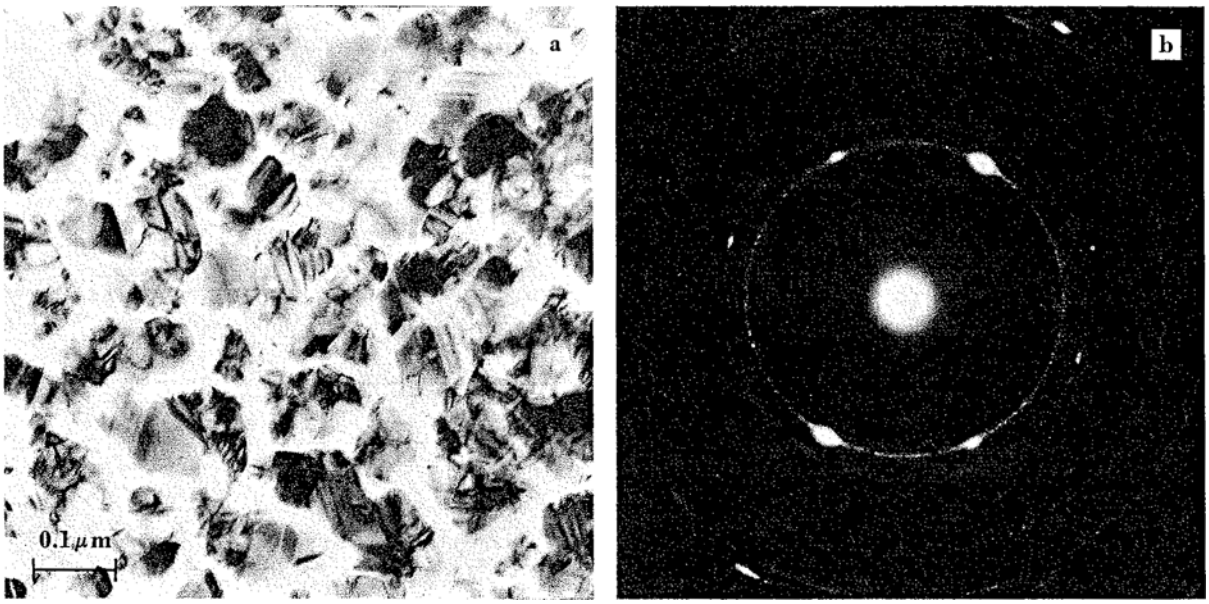

Fig. 11 Illustrating the corrosive disintegration of a 25 gold/75 silver atomic per cent alloy single crystal film in dilute nitric acid, (a) is a transmission electron micrograph showing deep channels parallel to the traces of twins formed during corrosion and (b) is the election diffraction pattern of this specimen showing the extensive misorientation of the small particles formed by corrosive disintegration

fringes spaced 1.8 nm apart and changes orientation by approximately 120° from one domain to another. The relative weakness of the extra diffraction spots and the low visibility of the interference fringes indicate that the corrosion phase is thin compared with the uncorroded alloy and probably extends not more than 5 nm below the corroded surface.

The structure of the corrosion phase cannot be identified unambiguously from the electron diffraction patterns, but it is thought to be an oxide of gold formed during the selective dissolution of silver from the alloy. Thus, we can expect the oxide — probably Au_2O_3 — to form within the near-surface disordered zone during corrosion of silver-rich alloys by strong acids. Gold(III) oxide (Au_2O_3) has an orthorhombic unit cell (19) with dimensions such that an epitaxial fit can be found with the fcc substrate of uncorroded alloy in three distinct crystallographic orientations, which is consistent with the tri-domain structure that is observed.

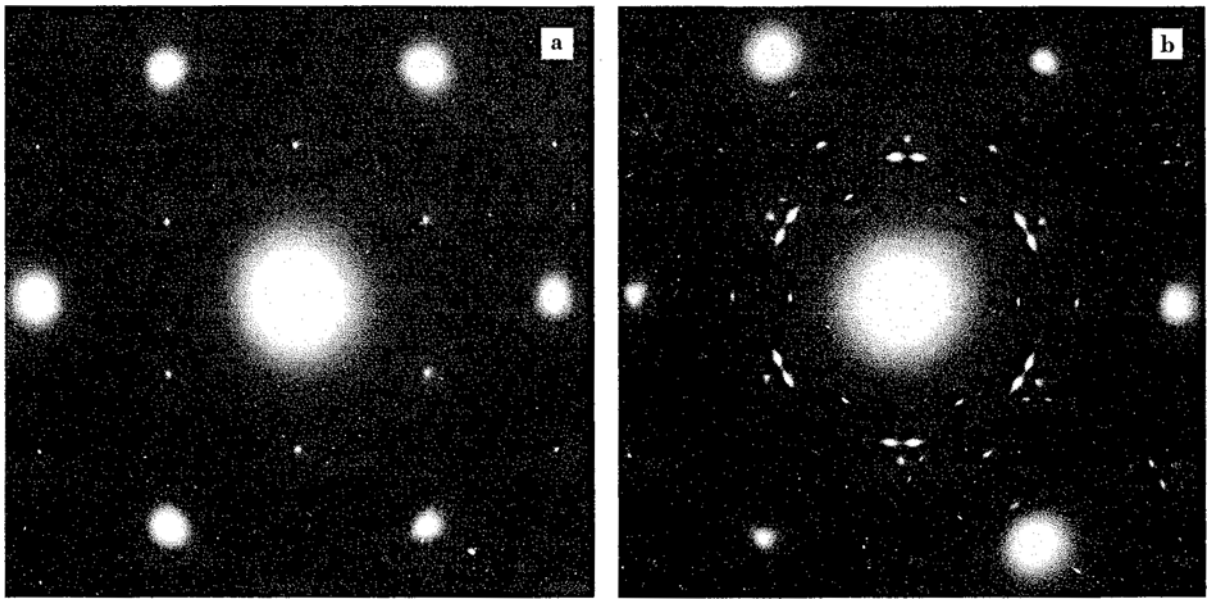

Fig. 12 Electron diffraction patterns of a 25 gold/75 silver atomic per cent alloy film, (a) before corrosion and (b) after corrosion in dilute nitric acid. The additional diffraction spots are due to the formation of a new phase

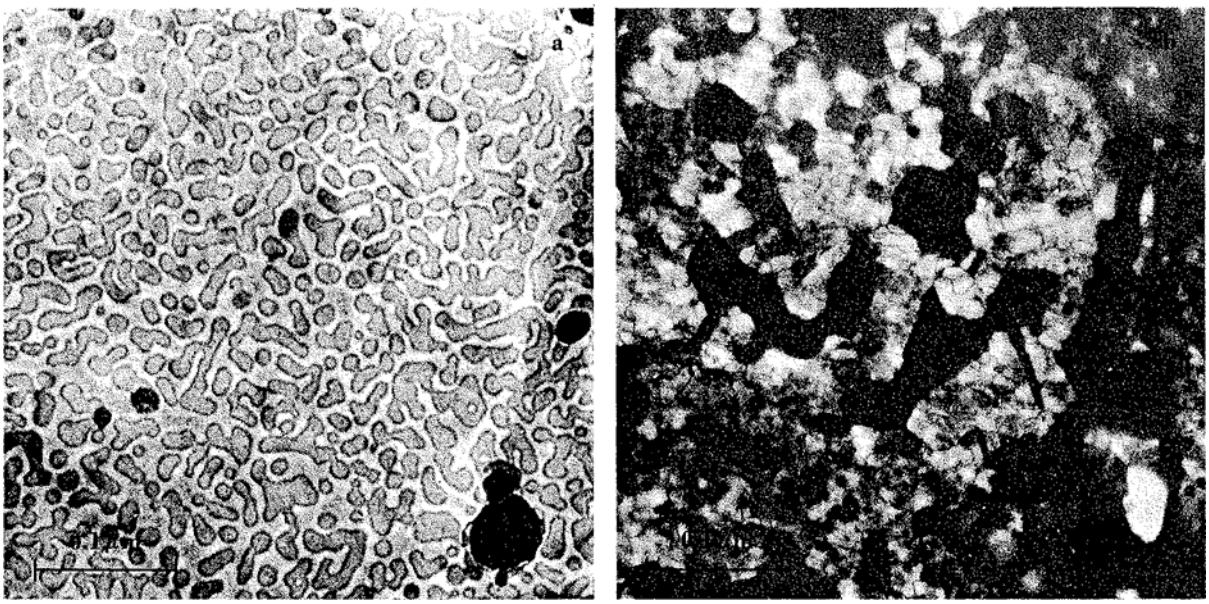

Fig. 13 Surface structure of a 25 gold/75 silver atomic per cent alloy film after corrosion in dilute nitric acid. (a) is a transmission electron micrograph using bright field illumination, showing island structures and (b) is the same area observed in dark field illumination using 'extra' spots in the diffraction pattern of Figure 12(b), thereby revealing surface domains of the 'corrosion phase'

The oxide formed under these corrosion conditions should be metastable, forming during the rapid dissolution of silver at the corrosion front, but tending to decompose when the silver dissolution is complete. Thus, a dynamic balance of the following processes:

Selective Dissolution→Gold Oxidation→Decomposition

might be established, with either the oxidation and/or the decomposition step predominating, depending on alloy composition and strength of acid. The decomposition of the oxide might be expected to occur preferentially at the oxide-acid interface, thereby yielding free gold atoms which can migrate across the surface, possibly assisted by partial ionization and solvation in the acid environment, to form the island morphology described earlier. In other words, island growth might be only a secondary result of the more important primary step of oxidation. This idea is supported by the observation that the rapid island growth found when the alloy is heated to 450°C after corrosion is accompanied by the simultaneous disappearance of the extra spots in the diffraction pattern. It seems possible, therefore, that island growth arises only as a result of oxidation followed by decomposition, as represented schematically in Figure 15.

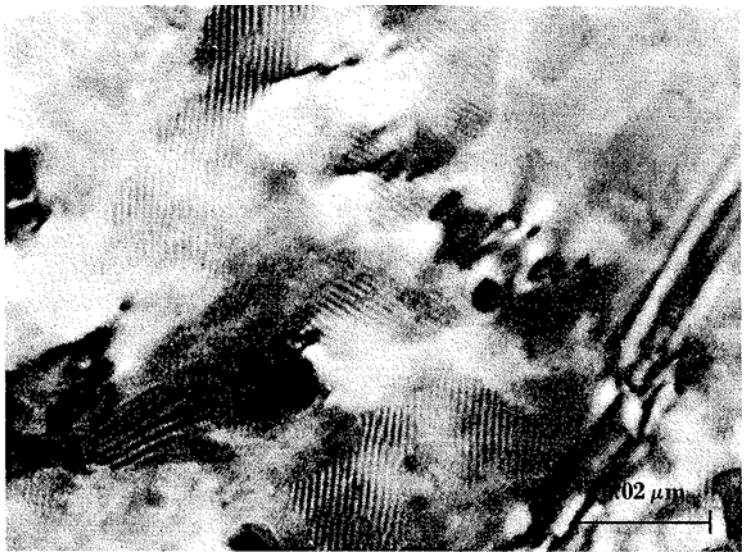

Fig. 14 High resolution transmission electron micrograph of a corroded 25 gold/75 silver atomic per cent alloy film, showing moiré-type interference fringes within the surface domains of the 'corrosion phase'

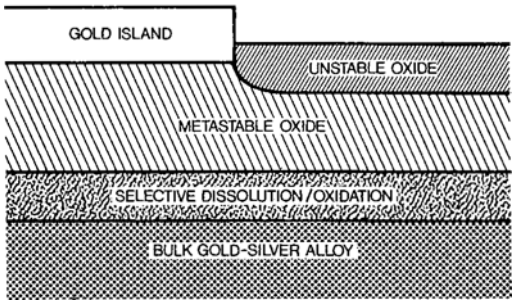

Fig. 15 Schematic representation of the corrosion of gold-silver alloys by selective dissolution accompanied by oxidation followed by decomposition of the oxide and island growth. Island growth eventually leads to pit formation and to tunnelling corrosion

Generalized Discussion

In this concluding section, we attempt to present a unifying review of the observations detailed in the foregoing, by means of a brief generalized discussion of the structural aspects of alloy corrosion by selective dissolution. The essential steps in the overall corrosion reaction are:

(1) Selective dissolution of the less noble species in the alloy
(2) Formation of surface vacancies and their inward migration
(3) Volume and surface diffusion
(4) Oxide formation
(5) Oxide decomposition.

Of these, some will be dominant and others may be absent, depending on the specific alloy and acid environment.

As we discussed at length at the beginning of this article, selective dissolution of the less noble component of an alloy should lead to the creation of surface vacancies. These can migrate across the surface to form pits, steps and other surface roughening features, or they can assist the migration of the residual noble metal atoms which leads to island growth; they can also diffuse into the underlying alloy to assist volume diffusion of the less noble metal to the corroding surface. According to Harrison and Wagner (20), a combination of surface and volume diffusion leads to a geometrical instability of the surface during selective dissolution. This may be important in establishing corrosion tunnels if a mechanism like that proposed by Swann is involved. On the other hand, if island growth resulting from surface diffusion is dominant, then the model for tunnelling proposed by Forty and Rowlands appears more realistic. Tunnelling is almost certainly always involved in the final stages of corrosive disintegration of an alloy.

The possibility of oxidation of the residual noble metal as a result of selective dissolution of the less noble metal has not previously been considered for gold alloys, although it has long been known that the selective dissolution of zinc from alpha-brass in ammoniacal solutions of suitable pH can be accompanied by a tarnishing reaction involving the oxidation of copper (21). It should be emphasized that the interpretation presented here of the electron diffraction patterns for the corrosion phase formed on gold-silver alloys by selective dissolution as evidence for oxidation is only tentative at this time. However, if oxidation of gold does occur under conditions of selective dissolution, it is likely to be a highly specific phenomenon, depending on the particular alloying component, rather than a general behaviour for all gold alloys. This probably accounts for the fact that the island morphology has so far been found as a regular feature only on gold-silver alloys. Clearly, the kinetics of the overall corrosion reaction leading eventually to dissolution by tunnelling must be dependent on whether or not the intermediate oxidation state occurs and, in turn, on whether this leads to island growth and, subsequently, tunnel formation.

Acknowledgements

Figures 2, 4, 5, 6, 7 and 8 have been published previously, as indicated in their captions. The writer is grateful to the authors and publishers of these articles for permission to include them here.

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